

## ABSTRACTS FROM THE ORIGINAL PAPERS.

*On the Buffer Action of Saké.*

by HIDEO KATAGIRI.

1. The acidity of Saké, estimated by the ordinary titration method varies depending upon the qualities and ages etc. from 0.12 % to 0.21 %. But when its  $P_H$  value was measured electrometrically, the difference between the maximum and minimum acidity was found to be far smaller than it is to be expected from the titration value. Thus according to the author's experiment, the  $P_H$  values of different samples of Saké collected from various districts of Japan, by the colorimetric method were from 3.7 to 3.9., while those by the electrometrical method, from 4.0 to 4.25. Even when Saké was diluted with water, two to five times its volume, the value remained nearly unaltered, still being between 4.0 and 4.25.

This phenomena were considered by the author was due to the high buffer action of the Saké solution. Consequently he investigated to find out, what constituents are exerting this action.

2. When Koji extract was fermented with Saké yeast, an increase in buffer action was always observed, thus showing that certain products possessing higher buffer action were formed during the fermentation process.

3. Saké was diluted with water from two to five times its volume, and the  $P_H$  values were determined either colorimetrically or electrometrically, then a measured quantity of decinormal hydrochloric acid or caustic soda solution was added in successively with an increasing quantity, and thus the  $P_H$  values were again determined after each addition, and the results obtained were shown as electro titration curves.

4. In the next experiments, each one of the chief constituents of Saké (i.e. alcohol, glucose, dextrin, glycerine, glycocoll, tyrosine, peptone, phosphates and

succinic acid etc.) was added to the diluted Saké solution, so as the concentration of that constituent in it become equal to that concentration in the original Saké solution, and the  $P_H$  values were determined before and after addition of either hydrochloric acid or alkali and the results were also given as titration curves. Any substance which has a greater buffer action must show a less deviation in the  $P_H$  values before and after the addition of either acid or alkali to it.

Comparing in this way the buffer action of the above mentioned constituents the author came to the following conclusions:—

- a) The addition of alcohol, glucose, dextrin or glycerine had no effect upon the buffer action and the titration curves before and after the addition of these substances remained nearly unaltered.
- b) Peptone, in such a low concentration as it presents in the original Saké solution, exerted no action.
- c) Glycocoll, more or less acted as a buffer against acid.
- d) Tyrosine, though present in a minute quantity, exhibited a distinct action of the buffer toward alkali.
- e) Phosphates had only a slight effect upon alkali.
- f) A most pronounced action was shown by succinic acid, and the addition of this acid only was enough to increase the strength of the buffer action as much as that in the original Saké solution.

After all, succinic acid played the most important rôle on the buffering action of Saké.

The author further discussed the relation between the sour taste given by Saké, and its  $P_H$  value and concluded that the strength of the sour taste is not always proportional to its  $P_H$  value, but certain unknown factors should be connected to it.

In the last chapter, the author has given a precise description of his experimental methods.

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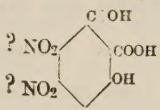
*On the Chemical Constitution of  $\beta$ -Acid Obtained by  
the Hydrolysis of Suzuki's Crude Oryzanin.*

By YOSHIKAZU SAHASHI.

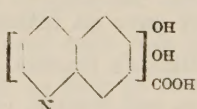
In 1912 Prof. U. Suzuki isolated two crystalline compounds from his crude oryzanin by boiling it with dilute acids, and he provisionally named them  $\alpha$ - and  $\beta$ -acids, respectively. The crude oryzanin was prepared from the alcoholic extracts of rice polishings, precipitating the extracts with phosphotungstic acid and then decomposing the precipitate with baryta in the usual way. When this crude oryzanin was boiled with 3% hydrochloric acid for about 2 hours, a brown resinous substance was formed on the surface of the liquid, which was filtered off while hot; and yellowish brown crystals that were formed on cooling the filtrate were collected, washed with water and recrystallized from hot alcohol. By fractional crystallization of the yellowish brown crystals, two kinds of crystals, i. e.  $\alpha$ - and  $\beta$ -acids were obtained. They had an acid reaction and were difficultly soluble in ether, in cold water, and in dilute acids, but were somewhat soluble in hot alcohol, and readily soluble in dilute alkali. They gave an intense reaction with diazobenzene sulphonic acid, and also a strong Millon's reaction. The empirical formulae  $C_{13}H_{16}N_2O_9$  and  $C_{10}H_8NO_4$  were given to  $\alpha$ - and  $\beta$ -acids, respectively; but his further investigations on the acids were interrupted, chiefly owing to the difficulty in preparing the material enough from crude oryzanin.

When the alcoholic extracts of rice polishings are dissolved in 20% alcohol and the solution allowed to stand for several weeks, a brown amorphous precipitate gradually settles down at the bottom. B. Suzuki has recently investigated this precipitate and found that a fair amount of  $\beta$ -acid would be formed, together with a brown resinous substance, by boiling this precipitate with dilute acids. The yield of the acid thus obtained was much better than that from crude oryzanin. (Jour. Chem. Soc. Japan, 1924). Consequently it has become much easier for the author to prepare a sufficient quantity of the acid by this method for his investigation. Many kilograms of the brown amorphous precipitate were supplied to the author from the Sankyo & Co, Tokyo, where oryzanin is manufactured in a large scale under the supervision of Prof. U. Suzuki, and thus the author was able to obtain more than 300 grams of  $\beta$ -acid in pure state, which was exactly identical with that obtained from crude oryzanin by Prof. Suzuki.

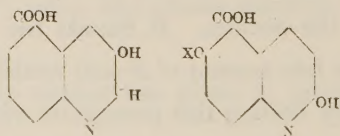
The author found that  $\beta$ -acid has one molecule of water of crystallization, which could hardly be removed at  $100^\circ\text{C}$ , but it was quite free from water when dried at  $150$ – $160^\circ$ . According to the results of the anhydrous sample it seemed to the author that  $\text{C}_{10}\text{H}_7\text{NO}_4$  would be more suitable for the formula of  $\beta$ -acid than  $\text{C}_{10}\text{H}_8\text{NO}_4$ , (that was) proposed by Prof. U. Suzuki. He dried his sample at  $100^\circ$  for analysis, therefore, it was probably not quite free from water. The author has prepared various compounds of this acid, i. e.  $\text{C}_{10}\text{H}_6\text{NO}_4\cdot\text{Na}$ ,  $\text{C}_{10}\text{H}_6\text{NO}_4\cdot\text{K}$ ,  $(\text{C}_{10}\text{H}_6\text{NO}_4)_2\text{Cu}$ ,  $(\text{C}_{10}\text{H}_6\text{NO}_4)_2\text{Ba}$ , and  $\text{Ag}$ -,  $\text{Ca}$ -,  $\text{NH}_4$ -salts, and also  $\text{C}_{10}\text{H}_6\text{NO}_4\cdot\text{CH}_3$ ,  $\text{C}_{10}\text{H}_8\text{NO}_4\cdot\text{C}_2\text{H}_5$ ,  $\text{C}_{10}\text{H}_7\text{NO}_4(\text{CO}\cdot\text{C}_3\text{H}_5)_3$ , etc. The formation of these salts and esters, proved it to be a monocarboxylic acid; while that of the benzoyl derivative confirmed the presence of two hydroxyl groups. Thus the formulae may be written as  $\text{C}_9\text{H}_7\text{N}(\text{OH})_2\text{COOH}$ .

When the  $\beta$  acid was treated with strong nitric acid, a dinitro-compound like juglonic acid , besides a fair amount of oxalic acid, was formed.

Finally, quinoline was obtained by zinc dust distillation of the  $\beta$ -acid, and this was identified by its picrate.

The author has thus concluded that  $\beta$ -acid is probably dihydroxy-quinoline carboxylic acid .

The relative position of  $(\text{OH})_2$  and  $\text{COOH}$  groups remains still under his investigation; but from the evidence of the formation of the dinitro-compound and oxalic acid, the author thinks that the  $\beta$ -acid will very likely have either one of the following formulae.





*A New Method of the Determination of the  
Water in Green Tea.*

By TOKITAKA SHIBA.

A cobalt chloride test-paper was prepared for the purpose of determining the water in green tea. Its preparation and application are very simple, and it can be used even by those who have no special knowledge of chemistry. This test-paper changes the colour shades according to the amount of the water present in the tea. The tea which does not change the blue colour of this test-paper No. 30 is suitable for preservation, that which changes (it) into red will change in its property, and the one which gives a violet colour can be kept only for a short period without changing its property. The test-paper can also be used in the quantitative determination of the water in tea, and the difference between the value obtained by the usual gravimetric method and that by the above method is about  $\pm 0.3$  per cent. With this test-paper the content of water can be determined in tea in any amount and in any vessel.

The sample of the standard of colour used does not last long, and so requires revision from time to time. The use of a table of the shades of colour painted with dye-stuffs is very convenient for a longer period of colour measurements, but it also requires the revision after some time.

The fact that this test-paper can be employed in determining the humidity of a room, where the tea is handled may be of very useful.

The method is, in the opinion of to the author, very profitable to prevent tea from the damage in its manufacture, caused by insufficient drying, which is easily avoided by its application.

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